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Zero point motion effect on the electronic properties of diamond, *trans*-polyacetylene and polyethylene

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Abstract. It has been recently shown, using *ab-initio* methods, that bulk diamond is characterized by a giant band–gap renormalization ($\sim 0.6\,\mathrm{eV}$) induced by the electron–phonon interaction. This result casts doubt on the accuracy of purely electronic calculations. In this work we show that in polymers, compared to bulk materials, due to the larger amplitude of the atomic vibrations the real excitations of the system are composed by entangled electron–phonon states. We prove as the charge carriers are fragmented in a multitude of polaronic states leading, inevitably, to the failure of the electronic picture. The presented results lead to a critical revision of the state–of–the–art description of carbon–based nanostructures, opening a wealth of potential implications.

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1 Introduction

The coupling between the electronic and atomic degrees of freedom plays a key role in several physical phenomena. For example it affects the temperature dependence of carriers mobility in organic devices [1] or the position and intensity of Raman peaks [2]. The electron-phonon coupling is also the driving force that causes excitons dissociation at the donor/acceptor interface in organic photovoltaic [3] and the transition to a superconducting phase in molecular solids [4]. From the theoretical point of view the role of the atomic vibrations has been treated in a semi-empirical manner for long. Such approach, based on model hamiltonians, relies on parameters that are difficult to extract from experiments. In contrast the *ab-initio* methods describe and in some cases predict in a quantitative manner the optical and electronic properties of electronic systems, without resorting to any external parameter. This goal is reached by benefiting of the predictivity and accuracy of density functional theory (DFT) [5] merged with many body perturbation theory (MBPT) [6]. Electronic properties are usually described within the so-called GW approximation [7], a purely electronic theory which allows to calculate corrections to the electronic levels with a high level of accuracy.

Many years ago [8], however, some pioneering works of Heine, Allen and Cardona (HAC) pointed to the fact that, even when the temperature vanishes, the effect of the electron-phonon coupling can induce corrections of the electronic levels, as large as the ones induced by correlation effects. The natural consequence is that a solely electronic theory may be inadequate leading to intrinsic errors as large as the precision of the *ab-initio* theories. Nevertheless, the enormous numerical difficulties connected with the calculation of the electron–phonon interaction, and the historical assumption that such interaction could lead only to minor corrections (order of few meV), has *de-facto* prevented the confirmation of the HAC predictions. As phonons are atomic vibrations, the effect of the electron-phonon coupling is usually associated to a temperature effect that vanishes as the temperature goes to zero. However this is not correct as the atoms posses an intrinsic spatial indetermination due to their quantum nature, even at zero temperature. This is the zero–point energy whose effect on the electronic properties is, generally, neglected.

Nowadays, the advent of more refined numerical techniques, has made possible to ground the HAC approach in a fully *ab-initio* framework. This has been used to compute the gap renormalization in carbon–nanotubes [9], the finite temperature optical properties of semiconductors and insulators [10], and to confirm a giant zero–point renormalization (615 meV) of the band–gap of bulk diamond [11], previously calculated by Zollner using semi–empirical methods [12]. These works are opening unpredictable scenarios connected with the actual accuracy of purely electronic theories and, thus, questioning decades of results.

The electronic theories ground on the concept of the single particle state: whatever is the external perturbation or internal correlation, the electron is still assumed to be characterized by a well defined energy, width and wave–function. As a consequence the charge–carriers are assumed to be mainly concentrated on electronic levels. The theoretical basis of the electronic concept is strictly connected with the quasi–particle (QP) concept [13] which assumes that the electron occupies a well–defined state, even if the electronic states are renormalized by correlation effects. Physically the electron is surrounded by a correlation cloud (composed by electron–hole pairs or phonons) whose effect, in the QP picture, reduces to an energy correction, a broadening of the electronic level, and a reduction of the effective electronic charge associated to the state.

In the past it has been shown that the electron-phonon coupling can break the quasi-particle approximation. In particular Scalapino et al. [14] predicted that in strong coupling superconductivity the Landau QP approximation is not valid, while Eiguren et al. [15] were able to reproduce the band splitting on a surface by a multiple quasi particle approximation.

More recently we have shown [16] that the quantum zero point motion of atoms induces strong dynamical effects on the electronic properties in diamond and *trans*-polyacetylene. The amplitude of the atomic vibrations and the consequent electron-phonon interaction leads an unexpected as well as striking result: the breakdown of the quasi-particle approximation. This result has been obtained by calculating the full *energy-dependent* spectral function (SF) of the electronic states, as reviewed in the second section. We interpreted the sub-gap states experimentally observed in diamond [17] and the formation of strong structures in *trans*-polyacetylene band structures in terms of entangled electron-phonon states. In this paper we extend these results to another polymer: the polyethylene. We will show that multiple structures appear in the SFs of the electronic states at $T = 0\,K$ and the bare electronic charge is fragmented in polaronic states, coherent packets of electrons and phonons, each corresponding to a peak in the SF. In the conclusions we will point out as these results represent an important step forward in the simulation of nanostructures, with a wealth of possible implications in the development of more refined theories of the electronic and atomic dynamics at the nano-scale.

2 Static and dynamical approach to the electron-phonon coupling

The HAC approach is a static theory of the electron-phonon coupling. It assumes that the scattering between the electrons and phonons is instantaneous. Dynamical effects are in fact connected to the retardation in the scattering between electrons and phonons and are generated by the time dependence of the atomic oscillations, $\mathbf{u}_{Is}$. Such retardation effects are normally neglected in the HAC theory but it is worth wondering, as the authors of Ref.[11] do in the case of diamond, if the agreement between theory and experiment can be somewhat fortuitous.

In the HAC approach it is possible to calculate the temperature dependent energy shift of the electronic state $\mid n\mathbf{k}\rangle$, with energy $\varepsilon_{n\mathbf{k}}$, induced by a configuration of static lattice displacements $\{\mathbf{u}_{Is}\}$

$$\Delta\varepsilon_{n\mathbf{k}}(T) = \sum_{\mathbf{q}\lambda} \frac{1}{N_{\mathbf{q}}} \sum_{n'} \left[\frac{\mid g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \mid^2}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}'}} - \frac{1}{2} \frac{\Lambda^{\mathbf{q}\lambda}_{nn'\mathbf{k}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}}} \right] \times \times (2B(\omega_{\mathbf{q}\lambda}) + 1)\,. \tag{1}$$

The key quantities in Eq. 1 are the Bose function distribution $B(\omega_{\mathbf{q}\lambda})$, the electron-phonon matrix elements $\mid g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \mid^2$ and the phonon frequencies $\omega_{\mathbf{q}\lambda}$. The last two quantities are calculated *ab-initio* using density functional perturbation theory [18]. The terms in Eq. (1) correspond to Fan and Debye-Waller corrections, in order of appearance. It must be noted that when the temperature vanishes the energy correction is not vanishing.

In the many body perturbation theory scheme, the electron-phonon self-energy is perturbatively calculated at the second order in the atomic displacements [6]. The electron-phonon self-energy is then composed of two contributions: the Fan self-energy

$$\Sigma^{Fan}_{n\mathbf{k}}(\omega) = \sum_{n'\mathbf{q}\lambda} \frac{\mid g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \mid^2}{N_{\mathbf{q}}} \left[\frac{B(\omega_{\mathbf{q}\lambda}) + 1 - f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \varepsilon_{n'\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}\lambda} - i0^+} + + \frac{B(\omega_{\mathbf{q}\lambda}) + f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \varepsilon_{n'\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}\lambda} - i0^+} \right] \tag{2}$$

and the frequency independent Debye-Waller term, $\Sigma^{DW}_{n\mathbf{k}}$. More details about the Debye-Waller term can be found, for example, in Ref. [12]. Subsequently the full frequency dependent Green's function $G_{n\mathbf{k}}(\omega)$ is readily defined to be

$$G_{n\mathbf{k}}(\omega) = \left(\omega - \varepsilon_{n\mathbf{k}} - \Sigma^{Fan}_{n\mathbf{k}}(\omega) - \Sigma^{DW}_{n\mathbf{k}}\right)^{-1}. \tag{3}$$

The single particle energies are obtained as poles of $G_{n\mathbf{k}}(\omega)$. The QP approximation is based on the assumption of a single pole in Eq. 3 due to the smooth ω-dependence of $\Re\Sigma^{Fan}_{n\mathbf{k}}$. As a consequence the QP energy is obtained by Taylor expanding $\Re\Sigma^{Fan}_{n\mathbf{k}}$ around the bare energy. In this way the Green's function is characterized by a single pole with energy

$$E_{n\mathbf{k}} \approx \varepsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\Re\Sigma^{Fan}_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}) + \Sigma^{DW}_{n\mathbf{k}}\,, \tag{4}$$

and the SF $A_{n\mathbf{k}}(\omega) \equiv \frac{1}{\pi}|\Im\left[G_{n\mathbf{k}}(\omega)\right]|$ is a Lorentzian function centered in $E_{n\mathbf{k}}$ with renormalization factor [6] $Z_{n\mathbf{k}} = \left(1 - \frac{\partial\Re\Sigma^{Fan}_{n\mathbf{k}}(\omega)}{\partial\omega}\Big|_{\omega=\varepsilon_{n\mathbf{k}}}\right)^{-1}$. The many body formulation represents the dynamical extension of the HAC approach, that is recovered from Eq. 2 under the condition $|\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}-\mathbf{q}}| \gg \omega_{\mathbf{q}\lambda}$ and the self-energy is static, implying $Z_{n\mathbf{k}} = 1$. The validity of this approximation is linked

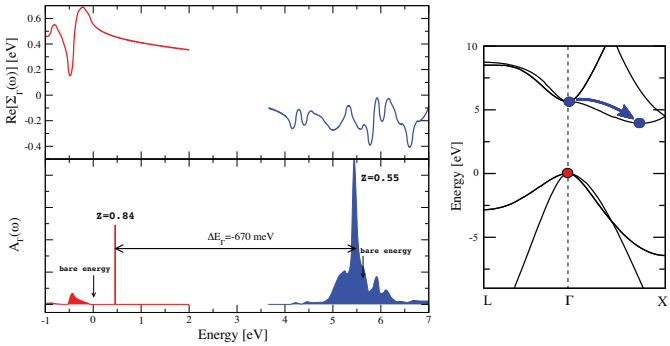

Fig. 1. The SFs of the Γ'_{25v} and Γ_{15c} states in bulk diamond, corresponding to the direct gap at Γ are shown. The bare energies are also indicated by the two vertical arrows. In the right frame the energy position of the two states are marked with spheres of the same color of the SFs. As the state Γ'_{25v} corresponds to the top of the valence bands the energy conservation forbids any relaxation mediated by the phonon modes. As a consequence the SF is very sharp. The SF of the conduction band, instead, acquires a wealth of additional structures besides the most prominent peak. These structures define a direct gap equal to 4.89 eV, 670 meV smaller than the bare LDA gap. The arrow in the right frame represent a typical relaxation process of the Γ_{15c} that causes the appearance of additional structures in the SF.

to the accuracy of the previous assumption or in other words: is the static approximation always accurate ?

In order to answer to this question we start to analyze the case of diamond. The static HAC theory predicts in this system a zero–point renormalization of the direct gap as large as 620 meV [19]. By using the full dynamical approach we calculated the SF of the Γ'_{25v} (red curve, left frame) and of the Γ_{15c} (blue curve, left frame) states, as shown in Fig. 1. If the static, HAC theory was exact we should see two delta–like peaks collecting all the electronic charge. On the other hand if the QP approximation was exact the two delta–peaks would broaden in two Lorentzian functions collecting most of the electronic charge, $Z_{n\mathbf{k}}$.

We notice immediately that the valence SF is characterized by a sharp peak shifted by 0.4 eV above the LDA value. This peak collects the 84% of the electronic charge, thus representing a genuine QP state. The energy correction of this state is well described in the HAC theory. The situation for the conduction state is, in contrast, drastically different. The state Γ_{15c} is not at the bottom of the conduction bands, as diamond is an indirect insulator. For this reason the electron placed in this state will undergo real transitions relaxing to lower energy states (blue arrow in the right frame of Fig. 1) and emitting phonons. As a consequence the imaginary part of the self–energy is more structured and, more importantly, the real part of $\Sigma_{\Gamma_{15c}}$ (left frame of Fig. 1) will be far from being frequency independent: the static approximation is bound to fail. Although a dominant peak is evident, this peak collects only the 55% of the electronic charge and additional less intense structures appear at lower energies causing the direct gap to shrink to 4.89 eV, 670 meV smaller than the bare LDA gap. Therefore the shrinking of the gap due to dynamical effects turns out to be 9 % larger then predicted in the HAC theory and in Ref. [11].

In general in semiconductors and insulators, the QP approximation is connected to the inverse of the plasmon energy, that gives the typical screening time. In most cases the plasmon energy is of the order of 10 eV, corresponding to a screening time of the order of 100 attoseconds. This time is shorter than the typical low–energy QP lifetimes (that are of the order of femtoseconds) and, as a consequence, the frequency dependence of the self–energy can be treated perturbatively. The shorter is the screening time, the more accurate is the QP approximation. In the limit of an extremely short screening time the static limit is recovered. In the case of the phonon mediated self-energy, Eq. 2, it is easy to show that the above arguments do not hold. The screening time is dictated by the Debye energy that is, at least, two orders of magnitude smaller then the plasma frequency. As a consequence phonon oscillations are much slower than the screening time, being of the order of femtoseconds. In the next section we will analyze in more details how these effects modify the electronic states in polymers, where coupling between electrons and ions is particularly strong.

3 Dynamical effects in nanostructures

A key difference between nanostructures and bulk materials is the reduced dimensionality. In simple terms this means that the atoms are more free to oscillate, thus inducing a potentially larger effect on the electronic dynamics. In addition, atomic vibrations are enhanced when the nanostructure contains light atoms as hydrogen. The different amplitude of the atomic vibrations can be easily visualized by using the phonon modes. Indeed, we can associate an average quantum size to each atom by using the standard variation σ_i^s of the atoms s along the direction i in the ground–state atomic wavefunction, at zero temperature. This is defined as $\sigma_i^s \approx \sqrt{\sum_{\mathbf{q}\lambda} (M_i \omega_{\mathbf{q}\lambda})^{-1} \left|\xi_i\left(\mathbf{q}\lambda\right)\right|^2}$, with $\xi_i\left(\mathbf{q}\lambda\right)$ the components of the polarization vector corresponding to the phonon momentum $\mathbf{q}$ and branch λ.

The different values of σ_i^s are pictorially showed in Fig. 2. In bulk diamond the carbon atom cloud has an isotropic wave–function and, consequently, the values of σ_i^s are independent on the direction. In *trans*-polyacetylene and polyethylene, the smaller distance between carbon atoms, reduces the standard deviation along the $\hat{x}$ direction. On the other hand, since hydrogen is much lighter than carbon, its standard deviation in the polymer plane is such that $\sigma^H \approx 0.2\, a.u.$. This points to a potential larger amplitude of the atomic oscillations with, consequently, a more pronounced electron-phonon interaction.

We investigate now the effect of such large atomic oscillations on the direct gap renormalization in *trans*-polyacetylene and polyethylene. In *trans*-polyacetylene the states corresponding to the extrema of the electronic bands are π/π^* orbitals. Since they are orthogonal to the plane where the polymer lies, electrons in these states are only

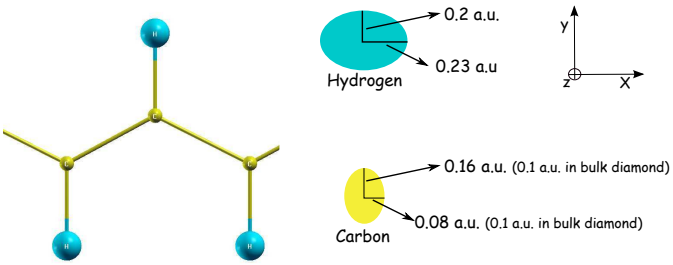

Fig. 2. The *trans*-polyacetylene structure is shown in the typical ball and stick representation. The standard deviations of the atomic wave–functions obtained with the harmonic approximation are also showed. The Hydrogen atom, on the average, has three times the deviation of the carbon atom, as expected from the different mass. Nevertheless the constraint imposed by the planar structure induces a similar "size" of the H and C atoms on the (x,y) plane. Compared to the bulk diamond case the carbon atom acquires, in the nanostructure, a double indetermination.

weakly affected by the in plane zero point atomic oscillations. An electron put at both the extrema of the bands in *trans*-polyacetylene, undergoes only virtual transitions not having any available final hole state. These transitions renormalize the electron energy and slightly broaden the electronic level, the SF is then dominated by a unique peak collecting about 99% of the electronic charge, as shown in the upper frame of Fig. 3. The distance between the two peaks is equal to 594 meV, pointing to a zero point renormalization of the electronic band gap of about 40 meV, with respect to the LDA value (634.5 meV). This value immediately reminds that one predicted by the static HAC theory in diamond. Nevertheless it points to a correction as large as 6% of the LDA band gap. A smaller correction with respect to the diamond case is ascribed to the peculiar electronic distribution of π/π^* orbitals.
Now we investigate the polyethylene case. The SFs of the states corresponding to its direct gap are shown in the bottom frame of Fig. 3. The SF of the top of the valence band is dominated by a sharp peak shifted of 280 meV with respect to the bare energy level. The peak of the bottom of the conduction band SF, is instead centered on the bare electronic energy. The resulting zero point renormalization of the gap is therefore 280 meV, larger than the *trans*-polyacetylene case. This points to the fact that when electrons are localized along the $C-C$ bond (in diamond and in polyethylene) the zero point motion effect on the renormalization of the electronic gap is sizable.

For what concerns the deeper states far from the gap, the effect of the electron-phonon coupling is stronger. In fact as they are in plane orbitals they are directly affected by in plane atomic vibrations. The SFs shown in Fig. 4 exhibit a wealth of structures and, as a consequence, are far from being assimilated to QP SFs. As we saw in diamond a so structured SF implies that the real part of the self-energy is far from being frequency independent. An electron put in a given state scatters with electrons and phonons in real transitions. This is correctly described by

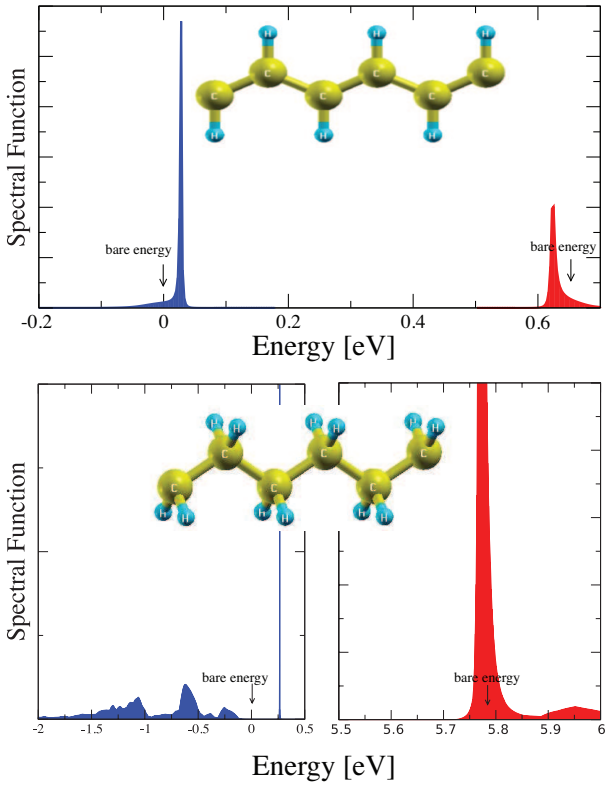

Fig. 3. The SFs of the states corresponding to the direct gap at X in *trans*-polyacetylene (upper frame) and at Γ in polyethylene (bottom frame). Since the extrema of the bands are π/π^* orbitals in *trans*-polyacetylene, the orthogonality of these orbitals points to a reduced electron-phonon interaction reflecting in very sharp SFs. In polyethylene the orbitals corresponding to the top of the valence and the bottom of conduction are spread along the bonds, in a similar way as happens in diamond. As a consequence the situation is different and additional structures appear in the SFs.

the dynamical theory of the electron-phonon coupling. As we can see from the Fig. 4 a multiplicity of structures appears in the SFs. Each of them picks up a fraction of the electronic charge $Z_{n\mathbf{k}}$ depriving the dominant peak of its weight. The trend for the deeper states is common both in *trans*-polyacetylene and in polyethylene. This is reasonable because both polymers have phonon frequencies of the same order of magnitude of the electronic excitations. Another crucial aspect is that some SFs overlap, like the 3^{rd}, the 4^{th} and the 5^{th} band in *trans*–polyacetylene. In this case it is impossible both to associate a single, well defined energy to the electron, and to state which band it belongs to. This is a signature of the breakdown of the band theory.

Critically looking at a given SF, for instance the state $\mid n=4, \mathbf{k}=\Gamma\rangle$ of *trans*-polyacetylene, two intense structures appear (Fig. 5).

As it is originally one electronic state $\mid n\mathbf{k}\rangle$, the two structures can not be assimilated to two distinct QPs, it would mean to associate to each peak one electron. In addition they are distant more than the Debye frequency

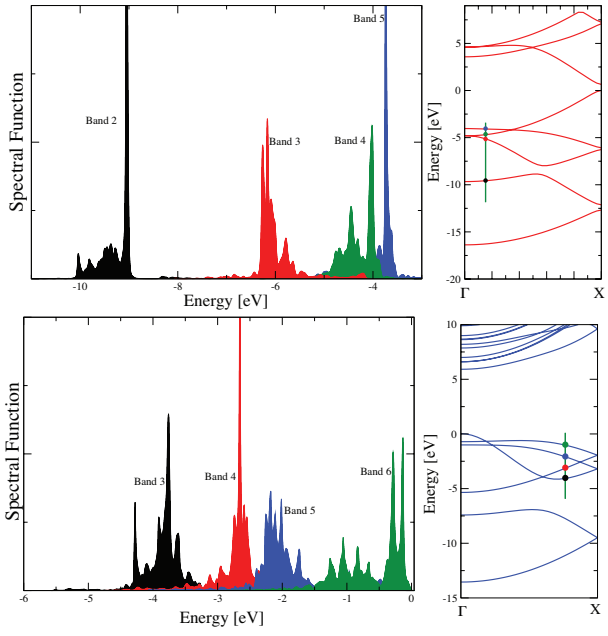

Fig. 4. The SFs of deeper states in *trans*-polyacetylene (upper frame) and polyethylene (bottom frame) are shown. The green lines in the right panels mark, at fixed **k** point, the energy range on which the corresponding SFs are shown. The energy position of the states shown in the left panel is marked by spheres of the same colour as the SFs. Since these states correspond to in plane orbitals they are strongly affected by the in plane atomic vibrations. The result is that the bare electronic levels are split in several polaronic states.

($\sim 0.4\,eV$) thus implies that they can not be simply interpreted as a main QP peak plus a phonon replica. Instead the formation of two peaks implies to consider an extended Fock space, composed of electrons and phonons. The breakdown of the quasiparticle picture is linked to the fact that the electron takes part in strong real transitions being its energy close to the poles of the self-energy. These scatterings send the bare electron into more than one of the mixed states of the extended Fock space (EFS), composed of electrons and phonons states. The stronger these scatterings are the more dressed the electron will be. As a consequence the electronic charge, $Z_{n\mathbf{k}}$, looses its physical meaning. The many body framework does not provide the tools to add further information about the composition of the "new" mixed states. The appropriate way is to remap the structures of the many-body SF to the solution of an eigenvalue problem in the electron-phonon EFS. In this framework the eigenstate of the system are

$$\mid I\mathbf{k}\rangle = \sum_{n} A^{I}_{n\mathbf{k}} \mid n\mathbf{k}\rangle + \sum_{n'\mathbf{q}\lambda} B_{n'\mathbf{k}-\mathbf{q}\lambda} \mid n'\mathbf{k}-\mathbf{q}\rangle \otimes \mid \mathbf{q}\lambda\rangle. \tag{5}$$

with energy $E_{n\mathbf{k}}$.

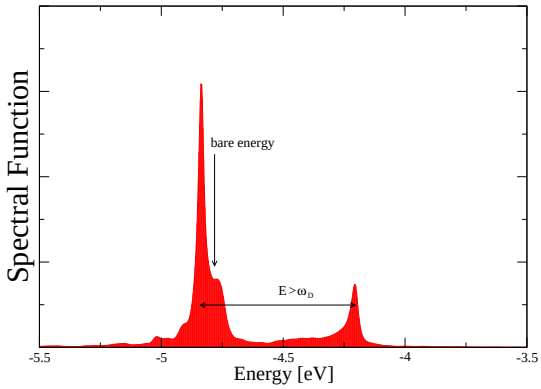

Fig. 5. The SF corresponding to the state $\mid 4, \mathbf{k} = \Gamma\rangle$ of *trans*-polyacetylene is shown. The position of the bare energy is indicated by a black arrow. The bare electronic level is mostly split into two polaronic states, which are more distant than the Debye frequency. For this reason they cannot be assimilated in terms of one electron plus a phonon replica.

$\mid A^{I}_{n\mathbf{k}} \mid^2$ is the probability to find the electron in the pure electronic $\mid n\mathbf{k}\rangle$ state. This reminds the physical meaning of the $Z_{n\mathbf{k}}$ factors, but in this contest the residual $\mid A^{I}_{n\mathbf{k}} \mid^2$ can not be assimilated to the electronic charge. $\mid B_{n'\mathbf{k}-\mathbf{q}} \mid^2$ is the probability that the polaronic state is in the mixed electron–phonon $\mid n'\mathbf{k}-\mathbf{q}\rangle \otimes \mid \mathbf{q}\lambda\rangle$ state.

In this way the existence of more than one structure in the SF can be interpreted in terms of more than one $\mid I\mathbf{k}\rangle$ projecting on the bare $\mid n\mathbf{k}\rangle$. In this way the shape of the spectral function is reproduced by weighting each eigenvalue of the mixed system by a Lorentzian broadening. In particular to each structure appearing in the SF calculated within the many body approach, is associated a precise state $\mid I\mathbf{k}\rangle$. Therefore the origin of the multiple poles in the spectral functions shown in Fig. 5 is connected to the existence of more than one intense state $\mid I\mathbf{k}\rangle$ belonging to the same state $\mid n\mathbf{k}\rangle$.

4 Conclusions

In this work we have shown that the HAC approach suffers of some limitations when we try to predict the zero temperature energy correction. Moreover the quantum zero point motion questions the reliability of the QP picture in diamond, *trans*-polyacetylene and polyethylene.

The SFs in fact exhibit multiple structures at $T = 0\,K$. The formation of additional structures suggests to consider the electron-phonon interaction in an extended Fock space composed by electrons and phonons. By mapping the structures of the many body SFs into the solution of an eigenvalue problem, it is possible to associate at each structure a particular polaronic state.

Because of its non perturbative nature, each polaronic state represents a coherent packet of electron–phonon pairs.

The cooperative dynamics between electrons and atoms rules out any description in terms of bare atoms, bare electronic states or quasiparticles.

The resulting coupled electronic and atomic dynamics pave the way for new investigations in polymers and more in general in low dimensional nanostructures. The cooperative dynamics of electrons and phonons in the polaronic states can have potential physical implications, as for example, an enhancement of the electronic mobility.

More generally the breakdown of the QP picture imposes a critical analysis of the previous results obtained using purely electronic theories.

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